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PREPARATION AND CRYSTAL STRUCTURE ANALYSIS OF DICHLORO[4-(DIMETHYLAMINO)-3,3-DIMETHYL-(*Z*)-BUT-1-EN-1-OL]-PALLADIUM(II), THE FIRST η^2-VINYL ALCOHOL COMPLEX OF PALLADIUM

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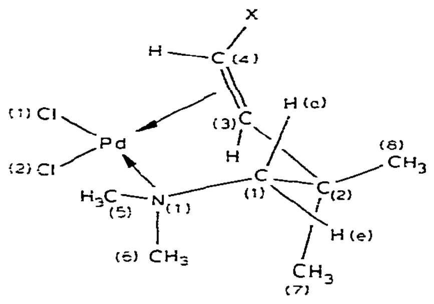
Summary

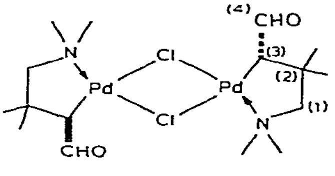
The first η^2-vinyl alcohol complex of palladium, $PdCl_2[Me_2NCH_2C(Me_2)\text{-}CH{=}CHOH]$, has been prepared and characterized by single crystal X-ray diffraction. Crystals are triclinic, space group $P\bar{1}$ with *a* 8.410(3), *b* 15.105(5), *c* 9.810(3) Å, α 90.88(1), β 102.89(1) and γ 95.62(1)°, $Z = 4$. The structure was solved by the heavy atom method and refined by full-matrix least-square calculations; $R = 0.052$ for 2531 reflexions with $I > 2\sigma(I)$. The two independent molecules have essentially the same conformations and dimensions; the only difference between them being in the orientation of the hydroxyl hydrogen. In each molecule the Pd coordination is close to square planar with *cis*-Cl atoms, and the C=C bond almost perpendicular to the plane. The five-membered chelate rings have envelope conformations with quaternary carbon C(2) at the flap; the configuration at the olefin bond is *cis*. There is a considerable *trans*-influence on the Pd—Cl bond lengths. Principal bond lengths are: Pd—Cl (*trans* to olefin) 2.342 and 2.357(3), Pd—Cl (*trans* to N) 2.292 and 2.296(3), Pd—N 2.069 and 2.072(8), Pd—C(3) 2.10 and 2.12(1), Pd—C(4) 2.26 and 2.27(1), C=C 1.37 and 1.41(2), C—O 1.31 and 1.32(1) Å.

Introduction

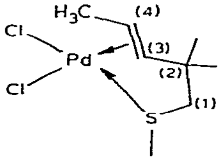
Vinyl alcohol complexes of palladium have not hitherto been isolated although such species are possible intermediates [1,2] in the palladium-catalysed oxidation of olefins to carbonyl compounds. Although vinyl alcohol complexes of platinum [3] and iron [4] have been characterised, some doubt has been expressed [5] as to whether analogous palladium compounds would have significant stability. While investigating the mechanism of the conversion [6] of



(I) X = H
(III) X = OH
(V) X = OMe



(II)



(IV)

dichloro[2,2,*N*,*N*-tetramethylbut-3-enylamine]palladium(II) (I) into di-μ-chlorobis[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-*C*,*N*]dipalladium(II) (II), ^{1}H NMR evidence suggested the intermediacy of a vinyl alcohol species. A complex of this type (III) has now been prepared by treating II with hydrogen chloride in acetone. Its spectral data are consistent with the chelated vinyl alcohol structure III including the *cis* stereochemistry of the double bond and the structure (Fig. 1) is unambiguously established by our X-ray analysis.

Experimental

Dichloro[4-(dimethylamino)-3,3-dimethyl-(Z)-but-1-en-1-ol]palladium(II)

Crystallization from acetone gave flat spars which, on standing under the solvent, were transformed into diamond-shaped prisms, m.p. 156—157°C (dec.); IR, ν_{max} (Nujol mull, thin polythene sheets supported by CsI plates) ca. 3180*v*(br) (OH), 1554s (C=C), 1071m (C—O), 970s (δ OH), 330m and 309m cm^{-1} (Pd—Cl); NMR: δ (CDCl$_3$) 1.20 (s, C—CH$_3$), 1.80 (s, C—CH$_3$), 2.26 (d, *J* 12.5 Hz, N—CH$_e$) (dd, *J* 12.5 and 1.5 Hz in CD$_3$COCD$_3$), 2.72 (s, N—CH$_3$), 2.99 (s, N—CH$_3$), 3.68 (d, *J* 12.5 Hz, N—CH$_a$), 4.59 (d, *J* 4.5 Hz, H(3)) (dd, *J* 4.5 and 1.5 Hz in CD$_3$COCD$_3$), 8.53 (d, *J* 4.5 Hz, H(4)).

Crystal data

$C_8H_{17}Cl_2NOPd$, mol.wt. 320.5, triclinic, *a* 8.410(3), *b* 15.105(5), *c* 9.810(3) Å, α 90.88(1), β 102.89(1), γ 95.02(1)°, *U* 1208.1 Å^3, $Z = 4$, D_c 1.76 g cm^{-3}, $F(000) = 680$. Mo radiation λ 0.71069 Å μ(Mo-K_α) 19.1 cm^{-1}. Space group *P*1 or $P\bar{1}$, $P\bar{1}$ assumed and confirmed by analysis. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12-reflexions (with θ in the range 10—20°) measured on a Hilger and Watts four-circle Y290 diffractometer. Intensity data were collected in our usual way [7] with a small (0.10 × 0.09 × 0.12 mm) crystal to a maximum θ of 25° and 3133 unique data were obtained. After corrections for Lorentz and polarization effects, the data with $I > 2\sigma(I)$ (2531) were labelled observed and used in structure solution and refinement. All calculations were carried out on the Amdahl V5 computer with our programs for data reduction. The SHELX [8] program system was used in subsequent calculations.

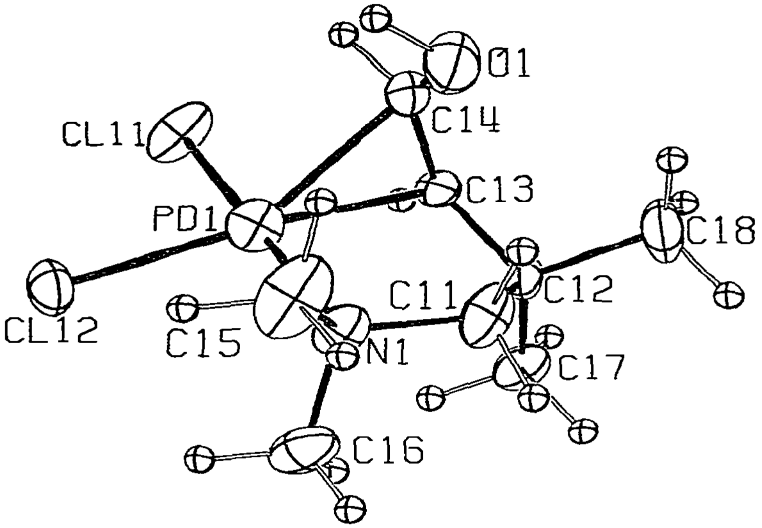


Fig. 1. View of molecule 1 of III showing the crystallographic numbering scheme *.

Structure solution and refinement

The coordinates of the Pd atoms were obtained from an analysis of a three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement by full-matrix least-squares calculations [8] initially with isotropic and then with anisotropic vibration parameters lowered $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ to 0.057. A difference map computed at this stage revealed maxima (0.3—0.6 e Å^{-3}) in positions expected for all the hydrogen atoms. The hydrogen atoms were allowed for in geometrically idealized positions (C—H, O—H, 1.08 Å, U_{iso} 0.059 Å^2) and included but not refined in the final rounds of calculations. In the final three refinement cycles a weighting scheme of the form $\sqrt{\omega} = 1/[\sigma^2 F + pF^2]^{1/2}$ was employed where the final p-parameter was 4.0×10^{-3}. Scattering factors used in the structure factor calculations were taken from references [9] and [10] and allowance was made for anomalous dispersion [11]. Refinement converged with $R = 0.052$ and $R\omega = [\Sigma\omega\Delta^2/\Sigma\omega F_0^2]^{1/2} = 0.060$ for the 2531 reflexions with $I > 2\sigma(I)$. A final difference map was devoid of any significant features. The max shift/error ratio in the last cycle was 0.48 for U_{22} of Pd(2) *.

Results

The molecular structure and atomic numbering scheme for one of the $PdCl_2(C_8H_{17}NO)$ (III) molecules is given in Fig. 1 which was prepared with the aid of

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* In III, the carbon atoms are numbered to correspond with those of I and II, although in the formal naming of the compound (see title) the carbon atom bearing the OH group has to be C(1). In the crystallographic discussion, for clarity, the numbering scheme in III is used and the two independent molecules we designate 1 and 2. For the crystallographic numbering scheme used in Table 1 and Fig. 1 the numbers 1 and 2 have been added to the atom labels, e.g. C(1) in molecule 1 is labelled C(11), C(1) in molecule 2 is labelled C(21), etc.

TABLE 1

FINAL FRACTIONAL COORDINATES (X10^4) FOR $C_8H_{17}Cl_2NOPd$ WITH STANDARD DEVIATIONS IN PARENTHESES

Molecule 1				Molecule 2			
Atom	x	y	z	Atom	x	y	z
Pd(1)	3408(1)	1147(0)	256(1)	Pd(2)	−95(1)	5580(0)	2719(1)
Cl(11)	1924(4)	−4(2)	−1176(3)	Cl(21)	−2843(4)	5148(2)	2424(4)
Cl(12)	4069(4)	1824(2)	−1705(3)	Cl(22)	313(4)	4132(2)	2037(3)
O(1)	5408(13)	282(7)	2803(9)	O(2)	910(11)	6638(5)	5492(8)
N(1)	4525(12)	2215(6)	1591(9)	N(2)	2335(11)	6046(6)	2861(9)
C(11)	4335(16)	2042(9)	3037(11)	C(21)	2629(15)	7046(7)	3273(11)
C(12)	2801(15)	1426(7)	3071(9)	C(22)	1128(16)	7525(7)	2839(11)
C(13)	2652(15)	648(7)	2049(11)	C(23)	−388(14)	6912(6)	3158(11)
C(14)	3946(21)	139(8)	1945(13)	C(24)	−360(14)	6538(7)	4428(11)
C(15)	6340(17)	2344(10)	1582(15)	C(25)	3431(17)	5548(9)	3917(13)
C(16)	3824(19)	3051(7)	1095(15)	C(26)	2749(17)	5868(9)	1464(12)
C(17)	1199(17)	1875(8)	2760(12)	C(27)	711(16)	7715(8)	1279(11)
C(18)	2942(24)	1034(12)	4587(11)	C(28)	1332(19)	8388(8)	3712(13)
H(1)	6347	191	2230	H(2)	474	6361	6377
H(111)	5403	1757	3610	H(211)	3039	7112	4398
H(112)	4231	2668	3539	H(212)	3568	7358	2794
H(131)	1465	479	1320	H(231)	−1468	6789	2345
H(141)	3677	−398	1147	H(241)	−1462	6149	4517
H(151)	6882	1746	1943	H(251)	3158	5655	4928
H(152)	6927	2900	2278	H(252)	4699	5781	3965
H(153)	6505	2470	539	H(253)	3218	4846	3628
H(161)	2527	2988	1069	H(261)	1981	6225	673
H(162)	4010	3170	56	H(262)	2541	5164	1190
H(163)	4432	3601	1796	H(263)	4021	6099	1527
H(171)	1038	2135	1724	H(271)	1722	8136	1043
H(172)	1277	2415	3515	H(272)	−389	8050	1025
H(173)	167	1399	2801	H(273)	529	7097	670
H(181)	4047	705	4868	H(281)	263	8745	3422
H(182)	1892	566	4610	H(282)	2389	8789	3520
H(183)	3002	1582	5323	H(283)	1537	8246	4810

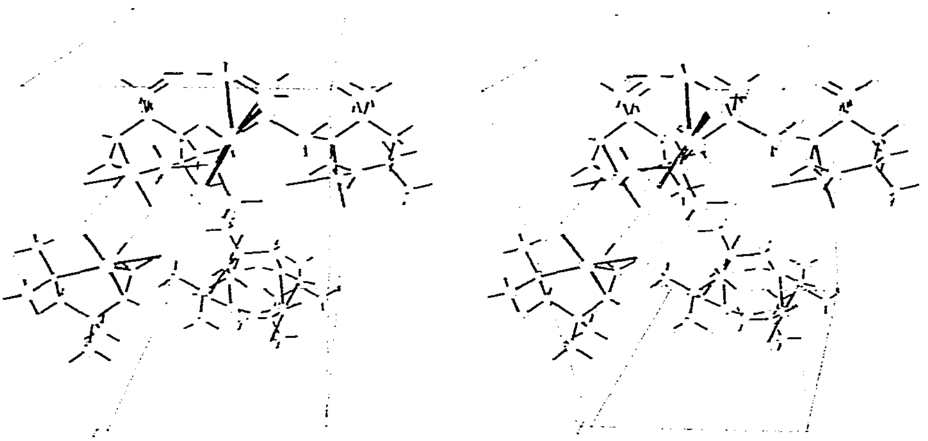

Fig. 2. Stereoview of the unit cell contents of III.

TABLE 2. INTERATOMIC DISTANCES (Å), ANGLES (°) AND TORSION ANGLES FOR (III).

	Molecule 1	Molecule 2
(a) Bond lengths		
Pd—Cl(1)	2.296(3)	2.292(3)
Pd—Cl(2)	2.342(3)	2.357(3)
Pd—N	2.072(8)	2.069(9)
Pd—C(3)	2.124(10)	2.101(10)
Pd—C(4)	2.268(11)	2.260(10)
N—C(1)	1.49(2)	1.54(1)
N—C(5)	1.52(2)	1.49(1)
N—C(6)	1.49(2)	1.51(1)
C(1)—C(2)	1.52(2)	1.50(2)
C(2)—C(3)	1.51(1)	1.59(2)
C(2)—C(7)	1.54(2)	1.53(1)
C(2)—C(8)	1.59(2)	1.52(2)
C(3)—C(4)	1.41(2)	1.37(2)
C(4)—O	1.32(2)	1.31(1)
(b) Angles		
Cl(1)—Pd—Cl(2)	89.4(1)	89.8(1)
Cl(1)—Pd—N	174.2(3)	175.3(2)
Cl(1)—Pd—C(3)	92.9(3)	92.5(3)
Cl(1)—Pd—C(4)	87.2(4)	87.0(3)
Cl(2)—Pd—N	93.1(3)	92.5(2)
Cl(2)—Pd—C(3)	173.8(3)	174.6(3)
Cl(2)—Pd—C(4)	148.7(4)	148.6(3)
N—Pd—C(3)	84.1(4)	84.9(4)
N—Pd—C(4)	93.5(4)	93.1(4)
C(3)—Pd—C(4)	37.4(5)	36.4(4)
Pd—N—C(1)	110.0(7)	110.3(6)
Pd—N—C(5)	109.0(7)	110.4(7)
Pd—N—C(6)	110.6(7)	108.4(7)
C(1)—N—C(5)	109.5(10)	109.5(9)

	Molecule 1	Molecule 2
C(1)—N—C(6)	110.7(10)	111.2(8)
C(5)—N—C(6)	107.0(10)	107.0(9)
N—C(1)—C(2)	112.9(9)	113.5(9)
C(1)—C(2)—C(3)	109.3(9)	108.0(8)
C(1)—C(2)—C(7)	114.7(10)	113.6(10)
C(1)—C(2)—C(8)	110.1(11)	109.6(10)
C(3)—C(2)—C(7)	109.5(9)	107.4(9)
C(3)—C(2)—C(8)	107.3(9)	107.8(10)
C(7)—C(2)—C(8)	105.7(10)	110.2(9)
Pd—C(3)—C(2)	107.3(7)	108.3(7)
Pd—C(3)—C(4)	76.9(6)	78.1(6)
C(2)—C(3)—C(4)	124.6(11)	122.9(10)
Pd—C(4)—C(3)	65.8(6)	65.4(6)
Pd—C(4)—O	115.0(9)	114.1(7)
C(3)—C(4)—O	122.0(11)	123.9(10)

(c) Hydrogen bond distances

O···Cl(1)	3.085	O···Cl(2)	3.041
H···Cl(1)	2.00	H···Cl(2)	1.95

(d) Torsion angles	Molecule 1	Molecule 2
C(3)—Pd—N—C(1)	3.7	3.6
Pd—N—C(1)—C(2)	—26.4	—27.2
N—C(1)—C(2)—C(3)	43.3	43.5
C(1)—C(2)—C(3)—Pd	—37.7	—37.8
C(2)—C(3)—Pd—N	19.0	19.5
C(2)—C(3)—C(4)—OH	—0.2	—1.7
N—Pd—C(3)—C(4)	—103.5	—103.4
N—Pd—C(4)—OH	—42.1	—42.9
C(3)—C(4)—O—H	—142	170

TABLE 3. MEAN PLANE DATA FOR $PdCl_2(C_8H_{17}NO)$

(Displacements (Å) of the atoms from the various planes. An * indicates that the atom was included in the plane equation calculation)

Atom	Plane 1			Plane 2			Plane 3		
	Molecule 1		Molecule 2	Molecule 1		Molecule 2	Molecule 1		Molecule 2
Pd	0	*	0	0.069	*	0.053	0.022	*	0.021
Cl(1)	—2.274		—2.263	—0.032	*	—0.025	—0.133		—0.086
Cl(2)	0.049		0.084	—0.002	*	—0.001	—0.158		—0.123
N	2.010		2.027	—0.036	*	—0.027	—0.030	*	—0.029
C(1)	2.392		2.392	—0.057		—0.034	0.026	*	0.025
C(2)	1.215		1.226	—0.628		—0.627	—0.526		—0.543
C(3)	0	*	0	—0.070		—0.067	0.017	*	—0.017
C(4)	0	*	0	1.263		1.241	1.230		1.279
Midpt. C(3)—C(4)				0.608		0.598			

Plane equations: in the form $aX + bY + cZ = d$ where X, Y and Z are the fractional coordinates given in Table 1

Plane 1	Molecule 1	$3.931X + 9.324Y + 4.285Z = 2.518$
	Molecule 2	$7.944X + 1.461Y + 0.418Z = 0.854$
Plane 2	Molecule 1	$7.269X - 8.383Y - 0.072Z = 1.445$
	Molecule 2	$-0.075X - 4.011Y - 9.325Z = 0.244$
Plane 3	Molecule 1	$7.157X - 8.411Y + 0.437Z = 1.464$
	Molecule 2	$-0.069X - 3.423Y + 9.405Z = 0.626$

ORTEP [12]. The other molecule in the asymmetric unit has an essentially identical conformation, the only difference being in the orientation of the hydroxyl hydrogen. Fig. 2 is a stereo pair showing the molecular packing. The final values of the positional parameters with their standard deviations are in Table 1 and Table 2 gives selected interatomic distances, bond angles and torsion angles. Table 3 gives details of mean plane calculations. A listing of the observed and calculated structure amplitudes and anisotropic thermal parameters is available from the authors on request.

Discussion

Our analysis establishes that vinyl alcohol complexes of palladium can be obtained in a stable form. The two independent molecules of III have essentially the same conformation in the solid state as shown by the torsion angle and bond length data (Table 2). The only significant difference between the two molecules is in the orientation of the hydroxyl hydrogen atom (Table 2) and this is caused by intermolecular hydrogen bonding. Each molecule is linked to form centrosymmetric dimers by O—H···Cl hydrogen bonds (O···Cl 3.041 and 3.085 Å). In one dimer the hydrogen bond involves the Cl atom *trans* to N whereas in the other it is the Cl atom *cis* to N that is utilized.

The palladium coordination is approximately square planar with *cis*-angles at Pd in the range 84.1—93.1(3)°. The five-membered chelate ring Pd, N, C(1), C(2), C(3) has an envelope conformation with the quaternary carbon atom C(2) at the flap and lying 0.53 Å (molecule 1) at 0.54 Å (molecule 2) from the best plane through Pd, N, C(1), C(3). Similar conformations have been found for the related chelate rings in II [6], IV [13] and V [14]. The Pd –Cl bond lengths (Table 2) show a marked *trans*-influence with those *trans* to olefin 0.05 to 0.06 Å longer than those *trans* to nitrogen.

The plane containing Pd and olefinic carbons C(3) and C(4) makes an angle 79.1° (molecule 1) and 78.6° (molecule 2) with the $PdCl_2N$ coordination plane. The Pd—olefin interaction is asymmetric with the mean Pd—C(3) distance (2.11(1) Å) much shorter than the mean Pd—C(4) distance (2.26(1) Å). The mid-point of the olefin bond is considerably above the $PdCl_2N$ plane (0.61 Å molecule 1, 0.60 Å molecule 2) and C(3) is only 0.07 Å below the $PdCl_2N$ plane in both molecules. An exactly analogous geometry has been reported for the Pt—olefin bond in $PtCl(acac)H_2C{=}CHOH$ [15] which has C=C 1.39(2) Å and vinylic C—O 1.30(1) Å not significantly different from those reported here for III (1.39(2) and 1.32(1) Å, respectively). Likewise, the metal—olefin interaction in III can be envisaged as being intermediate between that expected for a π-olefin complex and that found [6] in the σ-bonded aldehyde complex II. The remaining distances and angles in the ligand are not significantly different from those found in related systems [6].

Acknowledgements

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